

Ab initio phase diagram of BaTiO₃ under epitaxial strain revisited

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We revisit the phase diagram of BaTiO₃ under biaxial strain using a first principles-based effective Hamiltonian approach. We show that, in addition to the tetragonal (*c*), quasi-rhombohedral (*r*), and quasi-orthorhombic (*aa*) ferroelectric phases, that have been discussed previously, there are temperature and strain regions, in particular under tensile strain, where the system decomposes into multi-domain structures. In such cases, the strained system, at least on a local level, recovers the same phase sequence as the unclamped bulk material. Furthermore, we extend these results from the case of “uniform” biaxial strain to the situation where the two in-plane lattice constants are strained differently and show that similar considerations apply in this case.

The optimization of ferroelectric materials by epitaxial growth and interface-mediated strain is nowadays a well-established and highly successful method.¹ However, the experimental determination of strain-temperature phase diagrams is quite challenging, since only specific strain values, corresponding to the given lattice mismatch with a specific substrate, can be investigated. Therefore, the theoretical modeling of strain-dependent phase diagrams is highly relevant.

An important case is the prototypical ferroelectric BaTiO₃ (BTO), which, in its free bulk form, exhibits one paraelectric and three different ferroelectric structures as function of temperature,⁴ and thus gives rise to a rich strain dependence. Different levels of sophistication have been used to model/calculate the strain-dependent phase diagram of BTO, however, leading in part to conflicting results. First, various calculations based on Ginzburg-Landau-Devonshire theory have been performed, yielding qualitatively consistent phase diagrams as long as only mono-domain phases are taken into account.^{5,9} Once multi-domain configurations are considered, different (meta-) stable domain patterns have been found, depending on the *a priori* assumptions of the models.^{6,7} More recently, phase field simulations have been used in order to simulate different phases and domain structures without *a priori* assumptions.¹²

Both approaches, however, require parameters that have to be obtained from experimental data, and different choices for these parameters can lead to significantly different results.^{9,13} From this perspective, first principles-based calculations are very attractive, since in principle they do not require fitting. Indeed, first principles-based strain-temperature phase diagrams for BTO have been calculated,^{13–16} but only mono-domain states have been found for simulation cell sizes of about 12–16 unit cells along each cartesian direction.

Apart from determining the stability of different phases, the mechanical boundary conditions can also modify the domain pattern of the material. For example,

the formation of 90° domain walls provides an efficient way for tetragonal perovskites to partially relax the elastic energy under clamping to a periodic substrate.¹⁷ In PbTiO₃, such domain configurations have been predicted theoretically even without epitaxial constraints.¹⁸ In contrast, a rather large domain wall energy of 0.9 meV/Å² has been obtained for 90° domain walls in BTO,¹⁹ and it has been predicted that such domains are not stable for unclamped BTO.^{20,21} Experimentally, both multi-domain and mono-domain phases have been reported for BTO grown under tensile strain.^{22–24}

In the present paper, we show the presence of multi-domain states within a first principles-based effective Hamiltonian approach for sufficiently large simulation cells. For uniform biaxial tensile strain, the paraelectric phase first transforms to a multi-domain ferroelectric phase with local polarization along $\langle 100 \rangle$ and under further cooling a mono-domain state polarized along $\langle 110 \rangle$ is obtained. For small strains a multi-domain state with both in-plane and out-of-plane polarization is observed, while under compressive strain only mono-domain phases appear. Qualitatively the same trends are found for non-uniform biaxial strain, where a large variety of multi-domain states exist.

We use the feram code,²¹ which is based on the effective Hamiltonian discussed in Refs. 21, 25, and 26, and the parametrization given in Ref. 27. We perform molecular dynamics simulations in the canonical ensemble, employing a Nosé-Poincaré thermostat,²⁸ periodic boundary conditions, and a simulation box of 32×32×32 unit cells, i.e. corresponding to periodic images with about 13 nm distance. An ideal bulk material is modeled, without surfaces and depolarizing fields. To simulate the effect of epitaxial strain, the elements η_1 and η_2 of the homogeneous strain tensor (in standard Voigt notation) are fixed to the external strain η , and η_6 is set to zero. We define $\eta = 0$ corresponding to a lattice constant of 3.996 Å, as obtained within our approach for the free system directly above T_C . In the following, the two clamped in-plane directions are denoted as *a* and *b*, and the free out-of-plane direction as *c*.

Fig. 1 shows the calculated temperature dependence of the total electric polarization *P*, separated into in-plane

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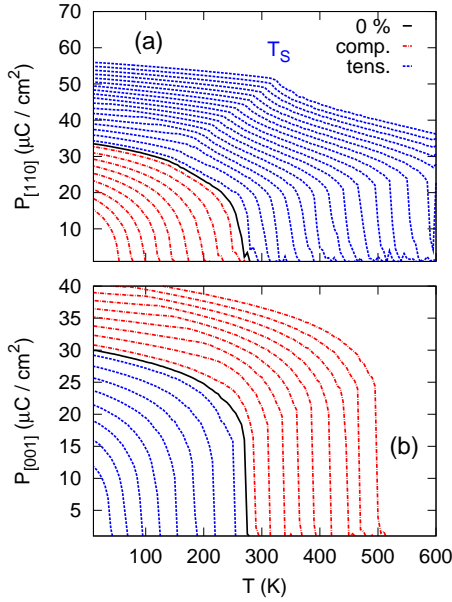


FIG. 1. (Color online) Calculated temperature-dependent polarization along (a) [110] and (b) [001] for different values of biaxial strain applied in the (001) plane (from -0.85% to $+1.75\%$ in steps of 0.1%). Solid (black) line: unstrained case ($\eta = 0$); Dashed (blue) lines: tensile strain; Dash-dotted (red) lines: compressive strain.

and out-of-plane components, for different values of the epitaxial strain ($\eta_a = \eta_b$). It can be seen that for zero strain both in-plane and out-of-plane components of P appear at the same temperature, while under compressive strain the appearance of the out-of-plane (in-plane) components are shifted to higher (lower) temperatures, and vice versa under tensile strain. This is in agreement with Ref. 13 and 16. However, we also observe that the temperature dependence of the in-plane polarization under tensile strain exhibits an unusual “kink-like” feature at a (strain-dependent) temperature T_S , somewhat below the overall critical temperature T_C .

Further inspection of the local soft mode configurations reveals that in the temperature range between T_C and T_S the system exhibits a multi-domain state, with average in-plane polarization along [110], but local in-plane polarization along [100] and [010], separated by 90° domain walls parallel to (110) (see Fig. 2(a)). Below T_S , the system adopts a mono-domain state with both local and global in-plane polarization along [110]. The formation of a multi-domain state under tensile strain allows the material to essentially recover the same phase sequence as in the free (unclamped) case, at least on a local level. At temperatures immediately below T_C , the tetragonal ferroelectric phase with polarization along $\langle 100 \rangle$ has the lowest free energy in the unclamped case.³⁰ However, a corresponding mono-domain state is strongly disfavored by the elastic boundary conditions introduced through the epitaxial constraint. Thus, by forming the observed multi-domain state, the system can lower its overall free

energy by achieving $\langle 100 \rangle$ polarization locally, at the cost of introducing energetically unfavorable domain walls. Thereby, the epitaxial constraint $\eta_a = \eta_b > 0$ promotes in-plane polarization with an equal volume fraction of [100] and [010] domains. However, for cell sizes below $20 \times 20 \times 20$, the energy penalty for forming domain walls exceeds the gain in free energy within the $\langle 100 \rangle$ -polarized domains, and consequently the multi-domain phase has been overlooked in previous *ab initio* simulations employing smaller simulation cells. Under further cooling, the $\langle 110 \rangle$ -polarized phase becomes more favorable, cf. Ref. 30 for the unclamped material, and thus a transition into a corresponding mono-domain state, which is also compatible with the epitaxial constraint under tensile strain, occurs at T_S .

For local $\langle 100 \rangle$ polarization, only 180° domain walls and 90° walls parallel to $\{110\}$ are possible by symmetry.²⁹ The latter type is indeed observed in our simulations (see Fig. 2(a)), whereas 180° domain walls do not relax any elastic energy and are thus not favorable in the present case. The polarization across the 90° domain wall can be separated into the nearly constant polarization perpendicular to the wall (P_\perp) and the polarization parallel to the wall (P_\parallel), which approximately follows a tanh-profile:^{19,29}

$$P_\parallel(x) = P_{0,\parallel} \tanh \left[\frac{x_N}{4\pi d_{DW}} \sin \left(\frac{4\pi}{x_N}(x - x_0) \right) \right], \quad (1)$$

with d_{DW} half of the domain wall width, x_0 center of one wall, $P_{0,\parallel}$ polarization in the domain center, x_N width of the fit region, and 4 the number of domains in the simulation cell (a minimum of 4 domains is necessary to match the domain profile at the periodic boundaries of the simulation cell). For $T = 400$ K and 0.75% tensile strain, the fit shown in Fig. 2(b) yields a domain wall width of about 5 nm, in good agreement with literature.^{19,29}

A clear signature of the multi-domain state in the temperature range between T_C and T_S can also be seen in various energy contributions, see Fig. 2(c). The modulation of P_\parallel and the elastic mismatch at the domain walls induce an energy penalty in the local mode self energy and the inhomogeneous part of the elastic energy, whereas the coupling energy between local strain and soft mode is reduced if the mono-domain state with P along $\langle 110 \rangle$ breaks up into multiple domains with local polarization along $\langle 100 \rangle$. We use these anomalies in the different energy contributions to identify T_C and T_S as function of strain and temperature. If no clear jump in energy is visible at T_C (due to the continuous character of this transition under strain),^{5,30} we instead use the lowest temperature with $P = 0$, which, however, gives rise to a large uncertainty of about 20 K.

Fig. 3 (a) illustrates the so-obtained phase diagram of BTO under uniform ($\eta_a = \eta_b$) biaxial strain. In qualitative agreement with previous work,^{13,16} we find two transition lines, T_C , corresponding to the appearance of in-plane and out-of-plane polarization, respectively, which cross for zero strain at the transition temperature of the

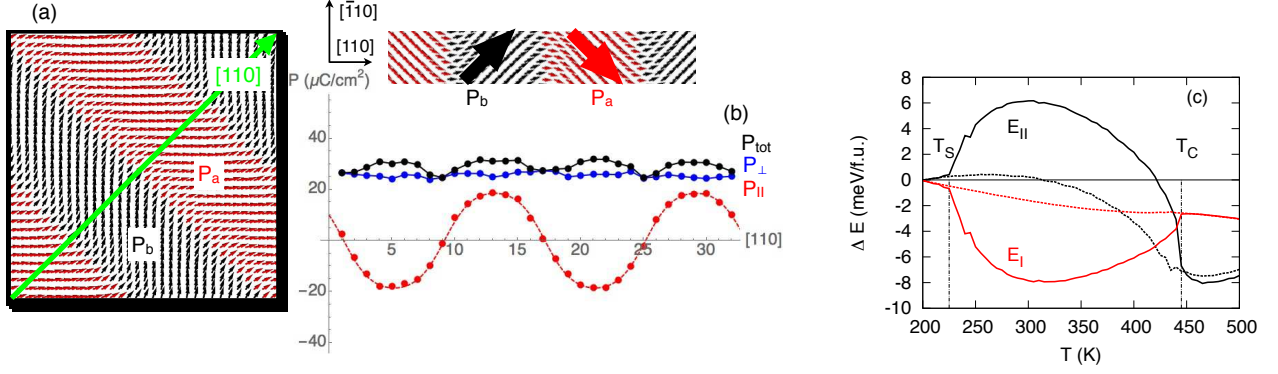


FIG. 2. (Color online) (a) Domain structure under 0.75% tensile epitaxial strain for $T_C > T = 400 \text{ K} > T_S$. Local dipole moments have been averaged along c and over 20 snapshots taken with a time distance of 0.2 ps. (b) Cross section of the polarization profile along $[110]$. Black: total polarization; Blue: P_{\perp} ; Red: P_{\parallel} , see text. Dashed line: fit to the domain profile given by Eq. (1). (c) Temperature dependence of selected energy contributions for $\eta = 0.75 \%$, normalized to 1 formula unit (f.u.) of BTO and taking the corresponding energy at 200 K as reference. Solid lines: case with multi-domain states ($32 \times 32 \times 32$ cell); dashed lines: mono-domain case ($16 \times 16 \times 16$ cell). E_I : coupling between soft mode and local strain; E_{II} : local soft mode energy and inhomogeneous part of the elastic energy. Vertical lines indicate T_C and T_S .

free bulk material. An additional transition line, T_S , separating multi-domain and single-domain phases is observed, extending from the tensile strain region into the region of small compressive strain. We note that T_S in Fig. 3(a) is still somewhat dependent on the used cell size (e.g. for $\eta = 0.75 \%$, T_S is reduced by 35 K when using a $92 \times 92 \times 92$ cell, while the the domain wall width is fully converged for a $48 \times 48 \times 48$ cell).

Below both in-plane and out-of plane T_C , we obtain a multi-domain region where the in-plane components of the polarization exhibit the same domain patterns as in the tensile strain region (see e.g. Fig. 2(a)), but with an additional uniform polarization component along c , resulting in 60° domain walls parallel to $\{110\}$. Thus, in this region the local and global polarizations are along $\langle 110 \rangle$ and $\langle 111 \rangle$, respectively. We note that down to $\eta = -0.45 \%$, the imposed strain acts as tensile strain relative to the shorter lattice constant of the tetragonal phase in the free material. For stronger compressive strain, T_S merges with the out-of-plane T_C and no multi-domain states are found.

The case of general biaxial strain (with $\eta_a \neq \eta_b$) is illustrated in Fig. 3 (b)-(g). Under cooling, first a local polarization along $\langle 100 \rangle$ (light, red regions) appears in most regions of the phase diagram, with P pointing towards the longest lattice direction (a or b for η_a or $\eta_b > 0$, c for compressive strain). The corresponding out-of-plane T_C decreases linearly with $\eta_a + \eta_b$, while the corresponding in-plane T_C increases linearly with the strain along the polarization direction, but is rather insensitive to the strain in the perpendicular direction. If two directions are under tensile strain, e.g. b and c for $\eta_a = -0.85 \%$ and $\eta_b = 0.35 \%$, a multi-domain state with local polarization along $\langle 100 \rangle$ and 90° domain walls is more favorable compared to a mono-domain state with polarization along $\langle 110 \rangle$. Thus, both mono- or multi-domain phases

with local polarization along $\langle 100 \rangle$ are found below T_C .

Under further cooling, local polarization along $\langle 110 \rangle$ (darker, blue) and then along $\langle 111 \rangle$ (black) becomes more favorable, analogously to the case of the free material. In general, the tendency for polarization along a certain direction increases, if the corresponding lattice constants in the clamped case are larger compared to their cubic, tetragonal, or orthorhombic counterparts in the free material. Thus, the transition into the $\langle 110 \rangle$ phases first sets in when both η_a and η_b are positive and for a combination of large compressive and weak tensile in-plane strains (leading to an elongation along c). Again, multi-domain states occur for a broad range of strains and temperatures. For local $\langle 110 \rangle$ polarization, 90° , 60° , and 120° domain walls are in principle possible.²⁹ As discussed above, only 60° domain walls parallel to $\{110\}$ with local ac and bc polarization are observed for $\eta_a = \eta_b$. For $\eta_a \neq \eta_b$, we find also 90° domain walls parallel to $\{100\}$ with local $ab/\bar{a}b$ or $ab/\bar{a}\bar{b}$ polarization and vanishing average global polarization along the shorter clamped lattice constant. For local $\langle 111 \rangle$ polarization, no multi-domain states are found for $\eta_a = \eta_b$. For $\eta_a \neq \eta_b$, 109° domain walls parallel to (010) and 71° walls parallel to (101) are possible,²⁹ and both types are found in our calculations. 71° walls occur for a combination of compressive and tensile strain and the corresponding local $abc/\bar{a}bc$ or $abc/\bar{a}\bar{b}\bar{c}$ polarization results in a vanishing global polarization along the compressed lattice constant. 109° walls with local $abc/\bar{a}\bar{b}\bar{c}$ or $abc/\bar{a}\bar{b}\bar{c}$ polarization, with neither net polarization along the shorter clamped lattice constant nor along c , are found for non-uniform tensile in-plane strain.

In summary, we have shown, using *ab initio*-based molecular dynamics simulations, that the phase diagram of BTO under biaxial strain shows a variety of multi-domain regions. The formation of domains allows the system to recover the same sequence of para- and ferro-

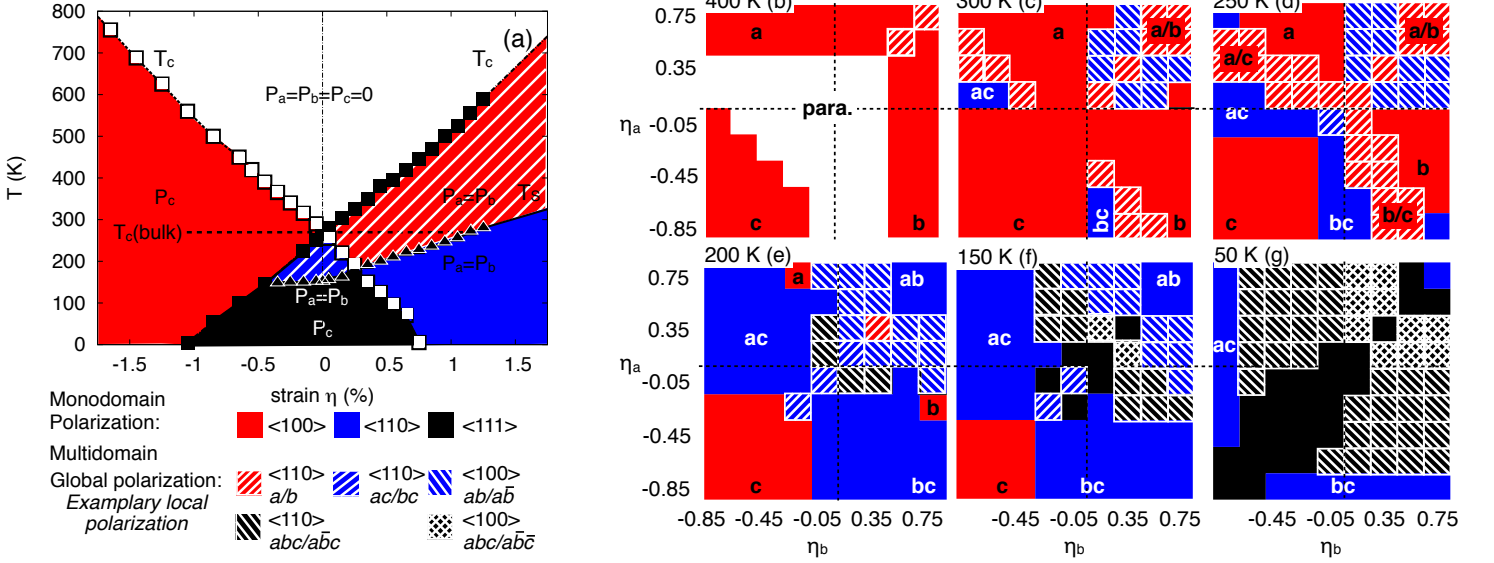


FIG. 3. (Color online) Phase diagram of BaTiO₃ under biaxial strain. Colors/grayscale encode the paraelectric (white) and ferroelectric phases with local polarization along $\langle 100 \rangle$ (red/light gray), $\langle 110 \rangle$ (blue/dark gray), and $\langle 111 \rangle$ (black). Multidomain configurations are indicated by striped regions as specified in the legend. (a) “Uniform” biaxial strain ($\eta_a = \eta_b$). Open (filled) squares indicate out-of-plane (in-plane) T_C , triangles indicate T_S . The horizontal dashed line indicates T_C for the free bulk material. (b)-(g) General biaxial strain with $\eta_a \neq \eta_b$ for different temperatures.

electric phases as in the unstrained bulk material (at least for most combinations of η_a and η_b), while simultaneously fulfilling all epitaxial constraints. Such multi-domain states have not been found in previous *ab initio*-based studies of strained BTO, due to restrictions in the size of the simulation cells. However, similar multi-domain configurations, have been observed in previous empirical phase-field simulations.¹² Our results thus consolidate to some extent the empirical with the *ab initio*-based simulations, and provide new insights for future studies and the better interpretation of experimental data in strained BTO films.

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¹D. G. Schlom, L.-Q. Chen, C.-B. Eom, K. M. Rabe, S. K. Streifer, and J.-M. Triscone, *Ann. Rev. Mater. Research* **37**, 586 (2007).

²D. G. Schlom, L.-Q. Chen, X. Pan, A. Schmehl, and M. A. Zurbuchen, *Journal of the American Ceramic Society* **91**, 2429 (2008).

³M. D. Biegalski, K. Dörr, D. H. Kim, and H. M. Christen, *Applied Physics Letters* **96**, 151905 (2010).

⁴T. Toshio, K.-H. Hellwege, H. Landolt, R. Börnstein, and O. Madelung, in *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology*, Group III, Vol. 3 (Springer, Berlin, 1981).

⁵N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).

⁶N. A. Pertsev and V. G. Koukhar, *Phys. Rev. Lett.* **84**, 3722 (2000).

⁷N. A. Pertsev, V. G. Koukhar, R. Waser, and S. Hoffmann, *Integrated ferroelectrics* **32**, 235 (2001).

⁸N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Ferroelectrics* **223**, 79 (2011).

⁹K. J. Choi, M. Biegalski, Y. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. Eom, *Science* **306**, 1005 (2004).

¹⁰Y. L. Li, S. Y. Hu, Z. K. Liu, and L. Q. Chen, *Applied Physics Letters* **78**, 3878 (2001).

¹¹Y. L. Li and L. Q. Chen, *Appl. Phys. Lett.* **88**, 072905 (2006).

¹²L.-Q. Chen, *Journal of the American Ceramic Society* **91**, 1835 (2008).

¹³O. Diéguez, S. Tinte, A. Antons, C. Bungaro, J. B. Neaton, K. M. Rabe, and D. Vanderbilt, *Phys. Rev. B* **69**, 212101 (2004).

¹⁴B.-K. Lai, I. Kornev, L. Bellaiche, and G. Salamo, *Appl. Phys. Lett.* **86**, 132904 (2005).

¹⁵J. Paul, T. Nishimatsu, Y. Kawazoe, and U. V. Waghmare, *Phys. Rev. Lett.* **99**, 077601 (2007).

¹⁶M. Marathe and C. Ederer, *App. Phys. Lett.* **104**, 212902 (2014).

¹⁷W. Pompe, X. Gong, Z. Suo, and J. S. Speck, *J. Appl. Phys.* **74**, 6012 (1993).

¹⁸S. Kouser, T. Nishimatsu, and U. V. Waghmare, *Phys. Rev. B* **88**, 064102 (2013).

¹⁹A. Grünebohm, M. E. Gruner, and P. Entel, *Ferroelectrics* **426**, 21 (2012).

²⁰T. Nishimatsu, K. Aoyagi, T. J. Konno, Y. Kawazoe, H. Funkauba, A. Kumar, and U. V. Waghmare, *J. Phys. Soc. Jpn.* **81**, 124702 (2012).

²¹T. Nishimatsu, U. V. Waghmare, Y. Kawazoe, and D. Vanderbilt, *Phys. Rev. B* **78**, 104104 (2008).

²²L. Qiao and X. Bi, *App. Phys. Lett.* **92**, 062912 (2008).

²³I. B. Misirliglu, S. P. Alpay, F. He, and B. O. Wells, *J. Appl. Phys.* **99**, 104103 (2006).

²⁴F. He and B. O. Wells, *Applied Physics Letters* **88**, 152908 (2006).

- ²⁵R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **49**, 5828 (1994).
- ²⁶W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B **52**, 6301 (1995).
- ²⁷T. Nishimatsu, M. Iwamoto, Y. Kawazoe, and U. V. Waghmare, Phys Rev B **82**, 134106 (2010).
- ²⁸S. D. Bond, B. J. Leimkuhler, and B. B. Laird, Journal of Computational Physics **151**, 114 (1999).
- ²⁹P. Marton, I. Rychetsky, and J. Hlinka, Phys. Rev. B **81**, 144125 (2010).
- ³⁰A. Kumar and U. V. Waghmare, Phys. Rev. B **82**, 054117 (2010).